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U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

09/601103

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/JP99/00768	February 22, 1999	February 23, 1998
TITLE OF INVENTION INFORMATION RECORDING MEDIUM		
APPLICANT(S) FOR DO/EO/US TAMURA, Reiji; WATANABE, Hitoshi; IKARI, Yoshihiro; TERAO, Motoyasu; MIYAGUCHI, Yasushi; *		
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:		
<p>1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.</p> <p>2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39.</p> <p>4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ul style="list-style-type: none"> a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). </p> <p>6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(3)).</p> <p>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(2)). <ul style="list-style-type: none"> a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input checked="" type="checkbox"/> have been transmitted by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input type="checkbox"/> have not been made and will not be made. </p> <p>8. <input checked="" type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</p> <p>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</p> <p>10. <input checked="" type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</p>		
Items 11. to 16. below concern document(s) or information included:		
<p>11. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98-1449 and International Search Report (PCT/ISA/210) w/ 8 references</p> <p>12. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</p> <p>13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.</p> <p>14. <input type="checkbox"/> A substitute specification.</p> <p>15. <input type="checkbox"/> A change of power of attorney and/or address letter.</p> <p>16. <input checked="" type="checkbox"/> Other items or information: <ul style="list-style-type: none"> 1.) International Preliminary Examination Report (PCT/IPEA/409)✓ 2.) Two (2) sheets of Formal Drawings ✓ </p>		

NEW 09/601103

PCT/JP99/00768

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17. The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5):**

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO. \$970.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$840.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO. \$690.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4). \$670.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4). \$96.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

Surcharge of \$130.00 for furnishing the oath or declaration later than 20 30 months from the earliest claimed priority date (37 CFR 1.492(e)).

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total Claims	8 - 20 =	0	X \$18.00	\$ 0
Independent Claims	1 - 3 =	0	X \$78.00	\$ 0
MULTIPLE DEPENDENT CLAIM(S) (if applicable)	None		+ \$260.00	\$ 0

TOTAL OF ABOVE CALCULATIONS = \$ 840.00

Reduction of $\frac{1}{2}$ for filing by small entity, if applicable. Verified Small Entity statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).

	SUBTOTAL =	\$ 840.00
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).	+	\$ 0

	TOTAL NATIONAL FEE =	\$ 840.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property	+	\$ 40.00

	TOTAL FEES ENCLOSED =	\$ 880.00
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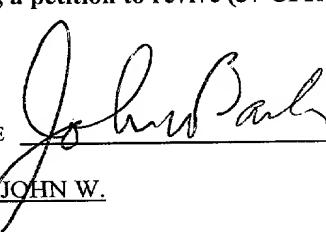
- a. A check in the amount of \$ 880.00 to cover the above fees is enclosed.
- b. Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 02-2448.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

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/cqc July 27, 2000

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PATENT
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IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicant: TAMURA, Reiji et al.

Int'l. Appl. No.: PCT/JP99/00768

Appl. No.: New Group:

Filed: July 27, 2000 Examiner:

For: INFORMATION RECORDING MEDIUM

PRELIMINARY AMENDMENT

BOX PATENT APPLICATION

Assistant Commissioner for Patents
Washington, DC 20231

July 27, 2000

Sir:

The following Preliminary Amendments and Remarks are respectfully submitted in connection with the above-identified application.

AMENDMENTS

IN THE SPECIFICATION:

Please amend the specification as follows:

Before line 1, insert --This application is the national phase under 35 U.S.C. § 371 of PCT International Application No. PCT/JP99/00768 which has an International filing date of February 22, 1999, which designated the United States of America.--

REMARKS

The specification has been amended to provide a cross-reference to the previously filed International Application.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37 C.F.R. § 1.16 or under 37 C.F.R. § 1.17; particularly, extension of time fees.

Respectfully submitted,

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DESCRIPTION

INFORMATION RECORDING MEDIUM

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Technical Field

The present invention relates to an information recording medium capable of recording digital information such as images, sounds and computer data with recording beams such as laser beams and electron beams.

Background Art

There are various principles for carrying out recording on thin films with laser beams, and the recording conducted by changing of atomic arrangement such as the phase change between crystal and amorphous substance causes substantially no deformation of the thin films and, hence, has the merit of being able to use a double-sided disk comprising two disks directly pasted together. Furthermore, by suitably selecting elements constituting the recording thin film and compositions of the thin film, rewriting of information can be performed, and, moreover, it becomes possible to carry out so-called direct overwriting, namely, overwriting a new information without erasing the previously recorded information. These recording films are already disclosed in JP-B-47-26897, etc., and the direct overwriting is disclosed in JP-A-62-259229, etc.

Furthermore, it has been known for a long time to form a protective film in contact with a recording film to inhibit deformation of the recording film, and it has been proposed to contain nitrogen in the protective film 5 to make the protective film denser and enhance the mechanical strength (JP-B-7-111786).

With a recent wide spread of the above-mentioned information recording media which carry out recording, erasing and reproduction of information by irradiation 10 with laser beams, namely, so-called optical disks, these are often used and stored in a severer environment. Thus, it is needed to improve reliability of optical disks more than before. From such a viewpoint, various environmental resistance tests have been conducted, and as a result, 15 there has been found a problem that when a disk in which an information has been once recorded is stored for a long time in a severe environment of high temperature and high humidity and then overwriting is carried out in the same portion as recorded, a writing error is caused. This is 20 examined in detail to find that the once recorded amorphous mark is not erased by the overwriting and remains. It is considered that this is because some changes in properties occur in the amorphous mark due to the leaving in a severe environment. Details of the 25 changes in properties are not clear, but they seem to include oxidation of the amorphous mark and aggregation of impurities present in the recording film. Thus, it is considered that the changes in properties hinder the

formation of crystal nuclei which play an important roll in the crystallization process (erasing process) of the amorphous mark, thereby causing failure in overwriting. In any way, that the once written information cannot be 5 rewritten means that information in file management area or defect management area can also be not rewritten, and this may cause serious troubles in the market.

Accordingly, the object of the present invention is to solve the above problems and provide an information 10 recording medium superior in reliability even in a severe environment.

Disclosure of Invention

As a result of intensive research conducted by 15 the inventors in an attempt to attain the object, it has been found that in an information recording medium having a construction comprising a recording film and a protective film formed in contact with the recording film, the state of the interface between the recording film and 20 the protective film is very important, and the above problems can be solved by taking into consideration the content of nitrogen around the interface.

That is, it has been found that in an information recording medium comprising a substrate on 25 which at least a recording film which undergoes change in atomic arrangement upon irradiation with recording beams and a protective film comprising a dielectric are formed in contact with each other, when contents of nitrogen on

both sides of the interface at which the recording film and the protective film contact with each other are allowed to differ from each other and when the changing amount of the nitrogen content in the direction of thickness of the film with the interface between the films as a boundary is 1-50 at.%/nm, the above problems can be completely solved.

As one embodiment, the nitrogen content on the recording film side is larger than that on the protective film side with the interface between the films as a boundary, and the nitrogen content in the recording film near the interface is larger than the nitrogen content in the inner part of the recording film. In this case, the recording film may comprise a layer of larger nitrogen content and a layer of smaller nitrogen content. Alternatively, the nitrogen content in the recording film may be such that it continuously decreases from the interface towards the inner part.

As another embodiment, the nitrogen content on the protective film side is larger than that on the recording film side with the interface between the films as a boundary, and the protective film contains as a main component a nitride of at least one of the elements constituting the recording film.

As further embodiment, the nitrogen content on the protective film side is larger than that on the recording film side with the interface between the films as a boundary, and the protective film contains a sulfide

as one of main components. In this case, the recording film preferably contains at least one element selected from Si, P, V, Mn, Fe, Co, Ni, Cu, Zn, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Sn, Ta, Os, Ir, Pt, Au, Tl, Pb, Bi and Cr. It is further preferred that the sulfide is zinc sulfide and the nitrogen content in the protective film is not more than 25 at.%. Content of at least one element selected from Si, P, V, Mn, Fe, Co, Ni, Cu, Zn, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Sn, Ta, Os, Ir, Pt, Au, Tl, Pb, Bi and Cr contained in the recording film is preferably 0.1-10 at.%.

Hitherto, it has been considered that formation of crystal nuclei more readily occurs in the area where composition abruptly or discontinuously changes, such as an interface between a recording film and a protective film, namely, so-called peculiar point, and an experimental fact has been known which supports the hypothesis that in a normal environment, the crystal nuclei are formed at the interface and crystal grows around the nuclei. However, as mentioned above, after left in a severe environment, the interface changes in properties, and there may occur a phenomenon that even if there is a discontinuity of the composition, the crystal nuclei are formed with difficulty and the crystallization does not proceed. On the other hand, it can be presumed that when the nitrogen content has a gradient of more than a certain level with the interface between the films as a boundary and the nitrogen content is abruptly changed as in the present invention, the changing point behaves as a

kind of peculiar point and not only accelerates the formation of crystal nuclei, but also keeps to have the effect to form the crystal nuclei at around the changing point even after left in a severe environment and thus failure in overwriting is inhibited.

On the other hand, in case the changing amount of the nitrogen content is increased with the interface between the films as a boundary, the change of the nitrogen content becomes more discontinuous, and, hence, formation of the crystal nuclei is further accelerated. In this case, failure in overwriting after left in a severe environment is not seen, but since the crystal nuclei are formed in excess, there is caused a problem that the once recorded information erases after left in a severe environment. Therefore, the gradient of the nitrogen content with the interface between the films as a boundary must be smaller than a certain value.

In view of the above, the inventors have been able to obtain a medium which causes no failure in overwriting and no erasing of information even if the medium is left in a severe environment and is excellent in reliability by adjusting the changing amount of the nitrogen content with the interface between the films as a boundary to 1-50 at.%/nm.

25

Brief Description of Drawings

FIG. 1 is a sectional view of the information recording medium obtained in Experimental Example 1 of the

present invention. FIG. 2 is a sectional view of the information recording medium obtained in Experimental Example 2 of the present invention. FIG. 3 is a sectional view of the information recording medium obtained in 5 Experimental Example 3 of the present invention.

Best Mode for Carrying Out the Invention

There are considered various methods for changing the nitrogen content with the interface between 10 the films as a boundary. The method of increasing the nitrogen content in the recording film than that in the protective film has the merit that the nitrogen content in the recording film can be relatively freely selected and the gradient of the nitrogen content with the interface 15 between the films as a boundary can be readily controlled. However, at the same time, there is caused a disadvantage that the melting point increases and the recording sensitivity lowers, and, thus, preferred is a method of containing nitrogen in only the recording film in the 20 vicinity of the interface between the recording film and the protective film. This method can easily control the gradient of the nitrogen content without causing deterioration of the recording sensitivity, and there are a method of forming a layer of large nitrogen content at 25 only the interface with the protective film and a method of continuously reducing the nitrogen content from the interface between the recording film and the protective film towards the inner part of the recording film. In the

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former method, thickness of the layer of large nitrogen content is preferably 1-5 nm. However, these methods have the defects that since the recording film comprises a multilayer, the film constitution becomes complicated and since the nitrogen content is continuously changed, the process becomes complicated.

In the case of increasing the nitrogen content in the protective film than that in the recording film, when at least one of the main components of the material forming the protective film is a nitride of the element constituting the recording film, the recording film and the protective film contain the same element, and thus there is the merit that the formation of crystal nuclei at the interface is readily accelerated. However, there is a defect that owing to an optical need that the protective film containing a nitride as a main component must be transparent to the laser wavelength for recording and reproduction, the nitrogen content is restricted to some extent and, hence, the gradient of the nitrogen content with the interface between the films as a boundary cannot be freely selected. Furthermore, the nitride is high in heat conductivity to cause a trouble of deterioration in recording sensitivity. In the case of using a nitride as the protective film, a construction which is optically transparent and less in restriction of the nitrogen content can be formed by continuously or discontinuously changing the nitrogen content in the vicinity of the interface and the content in the area apart from the

interface. Moreover, when a sulfide which is lower in heat conductivity than nitride is used as the material of the protective film, there is a merit that decrease of recording sensitivity is not brought about with ease. The sulfide is preferably zinc sulfide, and a mixture of zinc sulfide and silicon dioxide is lower in heat conductivity and is more preferred. However, when a material mainly composed of a sulfide is used as the protective film, there occur a phenomena that sulfur diffuses into the recording film by carrying out rewriting many times to cause increase of jitter. This phenomenon occurs more conspicuously in case nitrogen is contained in a large amount in the sulfide protective film. The reason for this deterioration is that optical constants of the recording film and crystallization rate change from the initial state due to the diffusion of sulfur. In this case, therefore, when elements which hardly cause diffusion of sulfur or do not deteriorate the optical constants or crystallization rate even if the diffusion occurs, namely, at least one element of Si, P, V, Mn, Fe, Co, Ni, Cu, Zn, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Sn, Ta, Os, Ir, Pt, Au, Tl, Pb, Bi and Cr, are contained in the recording film, the number of times of rewriting increases and this is preferred. These elements bond to the diffused sulfur to produce sulfides or to produce a barrier layer inhibiting the diffusion of sulfur, and thus have the effect to inhibit an adverse influence caused by the diffusion of sulfur. Of these elements, preferred are Co, Pd, Ag, Ta, Pt, Au, Tl

and Cr. Alternatively, when zinc sulfide is used as the sulfide protective film and the nitrogen content is adjusted to not more than 25 at.%, the diffusion of sulfur is difficult to occur and this is preferred. In the case 5 of adding to the recording film at least one of Si, P, V, Mn, Fe, Co, Ni, Cu, Zn, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Sn, Ta, Os, Ir, Pt, Au, Tl, Pb, Bi and Cr, if the amount of the element added is too large, the initial crystallization rate decreases, and, hence, the amount of the element is 10 preferably 0.1-10 at.%.

As the recording films, there may be used as main components the known materials such as Ge-Sb-Te based materials, In-Sb-Te based materials, Ag-In-Sb-Te based materials and In-Se based materials.

15

Examples

The present invention will be explained in detail by the following examples.

20 Experimental Example 1

A substrate 1 was prepared which comprised a polycarbonate resin sheet of 120 mm in diameter and 0.6 mm in thickness on the surface of which were previously formed embossed pits containing address information and 25 the like and U-shaped grooves of 0.74 μm in width and 65 nm in depth at a pitch of 1.48 μm . This substrate 1 was placed in the first sputtering chamber in a sputtering apparatus having a plurality of sputtering chambers and

excellent in formation of uniformity of film thickness and reproducibility. A $(\text{ZnS})_{80}(\text{SiO}_2)_{20}$ (mol%) first protective layer 2 having a thickness of 90 nm was formed using a mixture of ZnS and SiO₂ as a target in an argon gas. Then,
5 this substrate was transferred to the second sputtering chamber, and a chromium oxide interface film 3 having a thickness of 10 nm was formed in an argon gas using chromium oxide as a target. This interface film 3 had an effect to inhibit diffusion of S or the like in the first
10 protective film comprising ZnS-SiO₂. Furthermore, this substrate was transferred to the third sputtering chamber, and first an Ag-Ge-Sb-Te-N film (nitride recording film) 4 of 1 nm was formed using $\text{Ag}_{2.5}\text{Ge}_{20}\text{Sb}_{22.5}\text{Te}_{55}$ (at.%) sintered body as a target in a mixed gas of argon and nitrogen, and
15 then an $\text{Ag}_{2.5}\text{Ge}_{20}\text{Sb}_{22.5}\text{Te}_{55}$ (at.%) recording film 5 of 14 nm was formed with changing the gas to argon gas. The nitrogen content in the mixed gas used for the formation of the nitride recording film was 20 mol%. Then, the substrate was transferred to the fourth sputtering chamber
20 and a $(\text{ZnS})_{80}(\text{SiO}_2)_{20}$ (mol%) second protective layer 6 having a thickness of 15 nm was formed in the same manner as in the formation of the first protective layer. Then, an $\text{Al}_{94}\text{Cr}_6$ (at.%) first reflective layer 7 having a thickness of 68 nm was formed using an AlCr alloy as a
25 target in the fifth chamber. Finally, an $\text{Al}_{99}\text{Ti}_1$ (wt.%) second reflective layer 8 of 22 nm was formed using an AlTi alloy as a target in the sixth chamber. The laminate substrate was taken out from the sputtering apparatus, and

an ultraviolet curing resin protective layer 9 was formed by spin coating on the uppermost layer.

In the same manner as above, on another same substrate 1' were formed a $(\text{ZnS})_{80}(\text{SiO}_2)_{20}$ (mol%) first protective layer 2', a chromium oxide interface film 3', an Ag-Ge-Sb-Te-N film (nitride recording film) 4', an $\text{Ag}_{2.5}\text{Ge}_{20}\text{Sb}_{22.5}\text{Te}_{55}$ (at.%) recording film 5', a $(\text{ZnS})_{80}(\text{SiO}_2)_{20}$ (mol%) second protective layer 6', an $\text{Al}_{94}\text{Cr}_6$ (at.%) first reflective layer 7', an $\text{Al}_{99}\text{Ti}_1$ (wt.%) second reflective layer 8', and an ultraviolet curing resin protective layer 9'. The resulting two substrates were laminated with an adhesive layer 10 so that the ultraviolet curing resin layers 9 and 9' faced each other with the adhesive layer 10 therebetween. In this case, when the diameter of the adhesive layer was not less than 118 mm, the adhesive layer was hardly peeled by a shock such as falling.

The thus obtained disk was referred to as A1. In the case of the disk A1, the change of the nitrogen content with the interface between the nitride recording film and the protective film as a boundary can be changed by changing the nitrogen content in the argon-nitrogen mixed gas in the formation of the Ag-Ge-Sb-Te-N film (nitride recording film) 4.

25 Experimental Example 2

The same substrate 1 as of Experimental Example 1 was placed in the first sputtering chamber in a sputtering apparatus having a plurality of sputtering

chambers and excellent in formation of uniformity of film thickness and reproducibility. A $(\text{ZnS})_{80}(\text{SiO}_2)_{20}$ (mol%) first protective layer 2 having a thickness of 90 nm was formed in an argon gas using a mixture of ZnS and SiO₂ as a target. Then, this substrate was transferred to the second sputtering chamber, and a chromium oxide interface film 3 having a thickness of 20 nm was formed in an argon gas using chromium oxide as a target. This interface film 3 had an effect to inhibit diffusion of S or the like in the first protective film comprising ZnS-SiO₂. Furthermore, this substrate was transferred to the third sputtering chamber, and an $\text{Ag}_{2.5}\text{Ge}_{20}\text{Sb}_{22.5}\text{Te}_{55}$ (at.%) recording film 5 of 16 nm was formed in an argon gas using an $\text{Ag}_{2.5}\text{Ge}_{20}\text{Sb}_{22.5}\text{Te}_{55}$ (at.%) sintered body as a target. Then, the substrate was transferred to the fourth sputtering chamber and a Ta-N second protective layer 11 having a thickness of 18 nm was formed in a mixed gas of argon and nitrogen using a Ta-N sintered body as a target. The nitrogen content in the mixed gas was 40 mol%. Then, an $\text{Al}_{94}\text{Cr}_6$ (at.%) first reflective layer 7 of 35 nm was formed using an AlCr alloy as a target in the fifth chamber. Finally, an $\text{Al}_{99}\text{Ti}_1$ (wt.%) second reflective layer 8 of 35 nm was formed using an AlTi alloy as a target in the sixth chamber. The laminate substrate was taken out from the sputtering apparatus, and an ultraviolet curing resin protective layer 9 was formed by spin coating on the uppermost layer.

In the same manner as above, on another same substrate 1' were formed a $(\text{ZnS})_{80}(\text{SiO}_2)_{20}$ (mol%) first

protective layer 2', a chromium oxide interface film 3', an $\text{Ag}_{2.5}\text{Ge}_{20}\text{Sb}_{22.5}\text{Te}_{55}$ (at.%) recording film 5', a Ta-N second protective layer 11', an $\text{Al}_{94}\text{Cr}_6$ (at.%) first reflective layer 7', an $\text{Al}_{99}\text{Ti}_1$ (wt.%) second reflective layer 8', and 5 an ultraviolet curing resin protective layer 9'. The resulting two substrates were laminated with an adhesive layer 10 so that the ultraviolet curing resin layers 9 and 9' faced each other with the adhesive layer 10 therebetween. In this case, when the diameter of the 10 adhesive layer was not less than 118 mm, the adhesive layer was hardly peeled by a shock such as falling.

The thus obtained disk was referred to as A2. In the case of the disk A2, the change of the nitrogen content with the interface between the nitride recording 15 film and the protective film as a boundary can be changed by changing the nitride content in the argon-nitrogen mixed gas in the formation of the Ta-N second protective layer 11.

20 Experimental Example 3

The same substrate 1 as of Experimental Example 1 was placed in the first sputtering chamber in a sputtering apparatus having a plurality of sputtering chambers and excellent in formation of uniformity of film 25 thickness and reproducibility. A $(\text{ZnS})_{80}(\text{SiO}_2)_{20}$ (mol%) first protective layer 2 having a thickness of 90 nm was formed in an argon gas using a mixture of ZnS and SiO_2 as a target. Then, this substrate was transferred to the second

sputtering chamber, and a chromium oxide interface film 3 having a thickness of 20 nm was formed in an argon gas using chromium oxide as a target. This interface film 3 had an effect to inhibit diffusion of S or the like in the 5 first protective film comprising ZnS-SiO₂. Furthermore, this substrate was transferred to the third sputtering chamber, and an Ag_{2.5}Ge₂₀Sb_{22.5}Te₅₅ (at.%) recording film 5 of 16 nm was formed in an argon gas using an Ag_{2.5}Ge₂₀Sb_{22.5}Te₅₅ (at.%) sintered body as a target. Then, the substrate was 10 transferred to the fourth sputtering chamber and a ZnS-SiO₂-N second protective layer 12 having a thickness of 18 nm was formed in a mixed gas of argon and nitrogen using a mixture of ZnS and SiO₂ as a target. The nitrogen content in the mixed gas was 2 mol%. Then, an Al₉₄Cr₆ (at.%) first 15 reflective layer 7 of 35 nm was formed using an AlCr alloy as a target in the fifth chamber. Finally, an Al₉₉Ti₁ (wt.%) second reflective layer 8 of 35 nm was formed using an AlTi alloy as a target in the sixth chamber. The laminate substrate was taken out from the sputtering 20 apparatus, and an ultraviolet curing resin protective layer 9 was formed by spin coating on the uppermost layer.

In the same manner as above, on another same substrate 1' were formed a (ZnS)₈₀(SiO₂)₂₀ (mol%) first protective layer 2', a chromium oxide interface film 3', 25 an Ag_{2.5}Ge₂₀Sb_{22.5}Te₅₅ (at.%) recording film 5', a ZnS-SiO₂-N second protective layer 12', an Al₉₄Cr₆ (at.%) first reflective layer 7', an Al₉₉Ti₁ (wt.%) second reflective layer 8', and an ultraviolet curing resin protective layer

9'. The resulting two substrates were laminated with an adhesive layer 10 so that the ultraviolet curing resin layers 9 and 9' faced each other with the adhesive layer 10 therebetween. In this case, when the diameter of the 5 adhesive layer was not less than 118 mm, the adhesive layer was hardly peeled by a shock such as falling.

The thus obtained disk was referred to as A3. In the case of the disk A3, the change of the nitrogen content with the interface between the nitride recording 10 film and the protective film being a boundary can be changed by changing the nitrogen content in the argon-nitrogen mixed gas used in the formation of the ZnS-SiO₂-N second protective layer 11.

15 Comparative Example

A disk was prepared in the same manner as in the Experimental Example 1, except that in place of the ZnS-SiO₂-N film, a (ZnS)₈₀(SiO₂)₂₀ film was formed in the fourth sputtering chamber. This disk was referred to as B1.

20 Each of the resulting disks A1, A2, A3 and B1 was rotated at a linear speed of 6 m/s, and the recording film was irradiated through the substrate with semiconductor laser beams of 660 nm in wavelength condensed by an objective lens of NA 0.6 to perform 25 recording and reproduction. For recording, a waveform obtained by modulating the laser power between 11 mW and 5 mW, and a random signal modulated by 8-16 was recorded. A direct overwriting was conducted by forming a record mark

with a power of 11 mW and erasing it with a power of 5 mW. However, a multi pulse recording waveform which divides record pulse into a plurality of pulses was used other than for the shortest mark.

5 When a random signal was recorded in the above disks, jitter was not more than 8.5% in all disks. On the other hand, when data were recorded in these disks, these disks were left to stand for 500 hours in an environment of 80°C and 90%RH, then the same place as recorded was
10 subjected to direct overwriting with a random signal, and jitter was measured, a jitter of not more than 8.5% which was the same as before introduction into the environment in the disks A1, A2 and A3, but jitter was not less than 15% in the disk B1 and thus deterioration was seen in
15 overwriting characteristics.

Gradient of nitrogen content at the interface between the recording film and the protective film in each of the disks A1, A2, A3 and B1 was measured by Auger electron spectroscopy to obtain 3 at.%/nm in the disk A1,
20 30 at.%/nm in the disk A2, 7 at.%/nm in the disk A3, and 0 at.%/nm in the disk B1.

Conditions for forming films containing nitrogen in each of the disks A1, A2 and A3 were investigated, and each thirty disks for each of several kinds of disks
25 differing in change of the nitrogen content with the interface between the recording film and the protective film as a boundary were prepared. A random signal was recorded in all of these disks, and these disks were left

to stand for 500 hours in an environment of 80°C and 90%RH, then the same place as recorded was subjected to direct overwriting with random signal, and jitter was measured. In the case of the gradient of the nitrogen content being 5 0.5 at.%/nm, the jitter after overwriting exceeded 15% in not less than 10 disks of the disks A1, A2 and A3, respectively. However, in the case of 1 at.%/nm, 50 at.%/nm or 60 at.%/nm, the jitter after overwriting exceeded 15% in none of the disks. On the other hand, a 10 random signal was recorded in all of the disks, and these disks were left to stand for 500 hours in an environment of 80°C and 90%RH, then recorded data were reproduced and jitter was measured. In the case of 0.5 at.%/nm, 1 at.%/nm or 50 at.%/nm, the jitter exceeded 15% in none of the 15 disks, while in the case of 60 at.%/nm, the jitter exceeded 15% in not less than 10 disks of the respective disks. In the above experiments, the disks A2 in which the gradient of the nitrogen content at the interface was 0.5 at.%/nm and 1 at.%/nm had such construction that the 20 nitrogen content in the vicinity of the interface with the recording film was smaller than the nitrogen content in the inner part of the protective film.

The similar results were obtained in the disk A1 when, in the production of the disk, the nitrogen content 25 in the recording film was continuously changed by continuously changing the nitrogen content in the gas at the time of changing the sputtering gas from the mixed gas of argon and nitrogen to argon in the third sputtering

chamber.

Furthermore, the similar results were obtained when a part or the whole of Ag contained in the recording film is replaced with Si, P, V, Mn, Fe, Co, Ni, Cu, Zn, Nb, Mo, Ru, Rh, Pd, Cd, Sn, Ta, Os, Ir, Pt, Au, Tl, Pb, Bi and Cr. Among them, preferred are Co, Pd, Ta, Pt, Au, Tl and Cr. When amount of these elements was less than 0.1 at.%, the number of times of rewriting decreased. The effect of addition of these elements was most conspicuous in A3.

10 However, when the amount exceeded 10 at.%, the initial jitter became somewhat inferior.

The number of times of rewriting also decreased when the nitrogen content in the ZnS-SiO₂-N film in A3 exceeded 25 at.%.

15

Industrial Applicability

As explained above, according to the present invention, information recording media excellent in reliability of information even if left in a severe

20 environment could be obtained.

Claims

1. (Amended) An information recording medium comprising a substrate on which at least a recording film which undergoes change in atomic arrangement upon irradiation with recording beams and a protective film comprising a dielectric are formed, said recording film and said protective film being formed in contact with each other, wherein nitrogen contents on both sides of interface at which the recording film and the protective film contact with each other is such that the nitrogen content of the protective film side is greater than that of the recording film side and the changing amount of the nitrogen content in the direction of thickness of the film with the interface between the films as a boundary is 1-50 at.%/nm.

2. (Amended) An information recording medium according to claim 1, wherein the protective film contains a sulfide and the nitrogen content in the protective film is not more than 25 at.%, and the recording film contains an element which bonds to sulfur to form a sulfide or an element which produces a barrier layer inhibiting diffusion of sulfur.

3. (Amended) An information recording medium according to claim 2, wherein the recording film contains 0.1-10 at.% of at least one element selected from the group consisting of Si, P, V, Mn, Fe, Co, Ni, Cu, Zn, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Sn, Ta, Os, Ir, Pt, Au, Tl, Pb, Bi

and Cr.

4. (Amended) An information recording medium according to claim 2, wherein the recording film contains 0.1-10 at.% of at least one element selected from the group consisting of Co, Pd, Ag, Ta, Pt, Au, Tl and Cr.

5. (Amended) An information recording medium according to claim 2, wherein the recording film contains 0.1-10 at.% of Ag.

6. (Amended) An information recording medium according to claim 5, wherein the recording film contains Ge-Sb-Te based material.

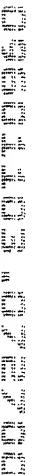
7. (Amended) An information recording medium according to claim 2, wherein the protective film contains zinc sulfide.

8. (Amended) An information recording medium according to claim 2, wherein the protective film contains a mixture of zinc sulfide and silicon dioxide.

9. (Deleted)

Abstract

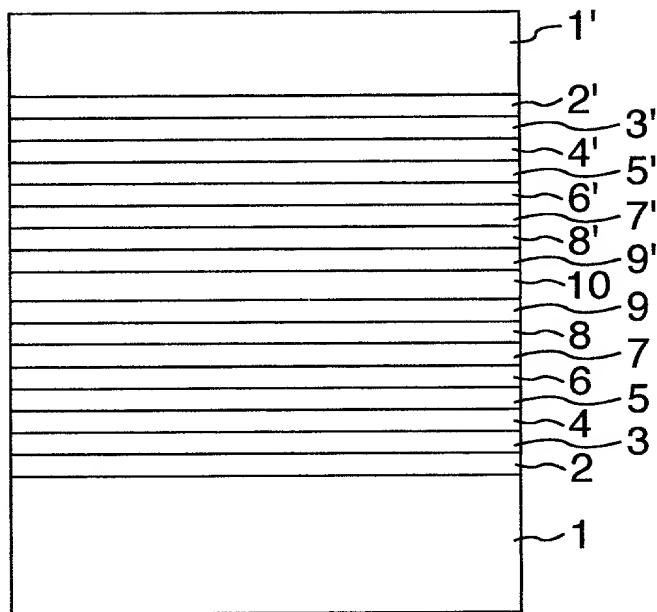
The object of the present invention is to obtain an information recording medium superior in recording and
5 reproducing characteristics and excellent in environmental resistance. According to the present invention, there is provided an information recording medium comprising a substrate on which are formed at least a recording film which undergoes change in atomic arrangement upon
10 irradiation with recording beams and a protective film comprising a dielectric, said recording film and said protective film being formed in contact with each other, wherein nitrogen content differs on both sides of the interface at which the recording film and the protective
15 film contact and the changing amount of the nitrogen content in the direction of thickness of the films with the interface between the films being a boundary is 1-50 at.%/nm.



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FIG.1



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FIG.2

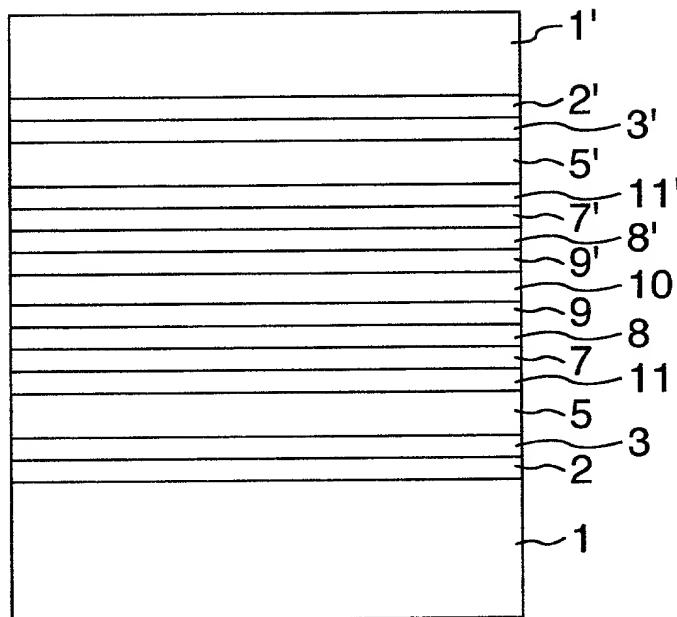
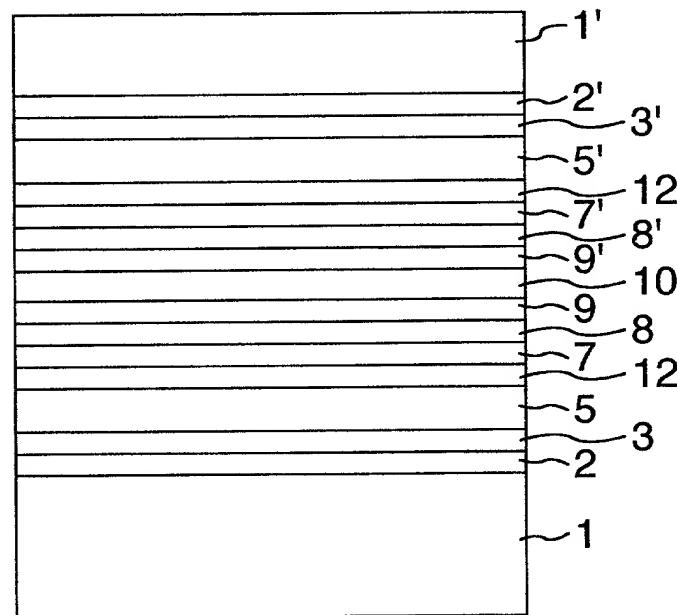


FIG.3



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ATTORNEY DOCKET NO.

152-531P

FOR PATENT AND DESIGN APPLICATIONS

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated next to my name; that I verily believe that I am the original, first and sole inventor (if only one inventor is named below) or an original, first and joint inventor (if plural inventors are named below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Insert Title:

"INFORMATION RECORDING MEDIUM"

Fill in Appropriate
Information -
For Use Without
Specification
Attached:

the specification of which is attached hereto. If not attached hereto,

the specification was filed on _____ as
United States Application Number _____; and / or

the specification was filed on February 22, 1999 as PCT
International Application Number PCT/JP99/00768; and was
amended under PCT Article 34 on September 22, 1999 (if applicable)

34

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I do not know and do not believe the same was ever known or used in the United States of America before my or our invention thereof, or patented or described in any printed publication in any country before my or our invention thereof or more than one year prior to this application, that the same was not in public use or on sale in the United States of America more than one year prior to this application, that the invention has not been patented or made the subject of an inventor's certificate issued before the date of this application in any country foreign to the United States of America on an application filed by me or my legal representatives or assigns more than twelve months (six months for designs) prior to this application, and that no application for patent or inventor's certificate on this invention has been filed in any country foreign to the United States of America prior to this application by me or my legal representatives or assigns, except as follows.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 (a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Insert Priority Information: (if appropriate)	Prior Foreign Application(s)			Priority Claimed	
	Number	Country	Month/Day/Year Filed		Yes No
	10-039976 (Number)	Japan (Country)	February 23, 1998 (Month/Day/Year Filed)	<input checked="" type="checkbox"/>	<input type="checkbox"/> Yes <input type="checkbox"/> No
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				<input type="checkbox"/>	<input type="checkbox"/> Yes <input type="checkbox"/> No
				<input type="checkbox"/>	<input type="checkbox"/> Yes <input type="checkbox"/> No
				<input type="checkbox"/>	<input type="checkbox"/> Yes <input type="checkbox"/> No

I hereby claim the benefit under Title 35, United States Code, §119(e) of any United States provisional application(s) listed below.

Insert Provisional
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(if any)

(Application Number) (Filing Date)
(Application Number) (Filing Date)

All Foreign Applications, if any, for any Patent or Inventor's Certificate Filed More Than 12 Months (6 Months for Designs) Prior To The Filing Date of This Application:

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Country Application No Date of Filing (Month/Day/Year)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

Insert Prior U.S.
Application(s):
(if any)

(Application Number)	(Filing Date)	(Status - patented, pending, abandoned)
(Application Number)	(Filing Date)	(Status - patented, pending, abandoned)

I hereby appoint the following attorneys to prosecute this application and/or an international application based on this application and to transact all business in the Patent and Trademark Office connected therewith and in connection with the resulting patent based on instructions received from the entity who first sent the application papers to the attorneys identified below, unless the inventor(s) or assignee provides said attorneys with a written notice to the contrary:

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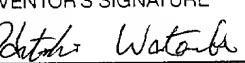
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

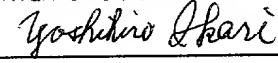
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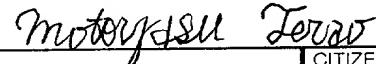
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* DATE OF SIGNATURE

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POST OFFICE ADDRESS (Complete Street Address including City, State & Country)			
GIVEN NAME	FAMILY NAME	INVENTOR'S SIGNATURE	DATE
RESIDENCE (City, State & Country)		CITIZENSHIP	
POST OFFICE ADDRESS (Complete Street Address including City, State & Country)			
GIVEN NAME	FAMILY NAME	INVENTOR'S SIGNATURE	DATE
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